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by

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# LITHOGRAPHY AND SPECTROSCOPY OF ULTRATHIN LANGMUIR-BLODGETT POLYMER FILMS

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Ultrathin (0.9 - 15.3 nm) poly(methylmethacrylate) (PMMA) and (30 - 40 nm) novolac/diazoquinone films prepared by the Langmuir-Blodgett (LB) technique have been explored as high-resolution electron beam resists and photoresists, respectively. One-eighth micron lines-and-spaces patterns have been achieved in PMMA using a Perkin Elmer MEBES I pattern generation system as the exposure tool. The etch resistance of PMMA films with thicknesses greater than 4.5 nm is sufficient to allow patterning of chromium film suitable for photomask fabrication. One micron lines-and-spaces patterns have been fabricated by optical lithography in 30 nm thick novolac/diazoquinone films, and etched into 50 nm of chromium. Monolayer PMMA films containing 5 mol% pyrenedodecanoic acid (PDA) as a probe were prepared by transfer to a quartz substrate at different surface pressures and characterized by fluorescence spectroscopy. The ratio of excimer to monomer emission intensity ( $I_e/I_m$ ) has a maximum value at  $\sim 10$  dyn/cm, which is suggestive of a structural rearrangement occurring in the Langmuir film at that surface pressure.

## Introduction

As the dimensions of integrated circuits keep shrinking, the desired resolution will soon be beyond the limit of conventional ultraviolet (UV) lithography. Deep UV and X- radiation, high and low energy electron beams and scanning tunneling microscopy (STM) have been proposed (1) as possible exposure systems for the next generation high resolution lithography. In optical lithography (UV or DUV) the resolution is limited by resist absorption, light diffraction, and rheological effects related to the resist development process. In electron beam lithography the

major limitation on the resolution is imposed by electron scattering (proximity effect), which causes a nonuniform incident exposure in the pattern area. These resolution limiting effects generally become more serious with increasing resist thickness. Therefore, to improve the resolution in both optical and electron beam lithography, the use of ultrathin resists (with thicknesses  $< 200$  nm) has been proposed (2-8).

Ultrathin resists have many technological advantages: In optical lithography they offer improved exposure and focus latitude (9), and alleviate the problem of absorption in conventional resists, such as novolac, especially for deep UV exposure. In electron-beam lithography the use of ultrathin resists will reduce electron scattering within the resists and thus make the proximity effect correction schemes (10) easier to implement. The most attractive advantage of an ultrathin resist is that it allows for electron penetration when the scanning tunneling microscope (STM) is used as a very low voltage exposure tool (1). Because the STM is capable of creating patterns with extremely high resolution ( $< 10$  nm) and potentially at very high speed, it may become an important lithographic tool in the near future with the use of ultrathin polymer films as resist materials.

To prepare ultrathin polymer films on the surface of wafers, especially those of large diameter (6 or 8 inch), uniformity and defect density become important factors in determining the resist quality. The conventional spin coating method has been reported to introduce interference striations (11) and high defect densities (2,3) when used to prepare ultrathin polymer films. As an alternative approach, the LB technique has been proposed as being suited to the preparation of more uniform ultrathin polymer films (2). Using this technique monolayer polymer films can be transferred layer by layer to the surface of a solid substrate from the water surface. An important feature of the LB technique is that the accumulation of monolayer films allows the thickness of the built-up film to be controlled in a precise manner. Consequently, extremely uniform and ultrathin polymer films can be prepared.

In order to establish a basis for rationalizing the lithographic performance of ultrathin polymer films, a better understanding of their structure at the molecular level is required.



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However, to date there has been very little effort in this area (12-14). Ultrathin polymer films prepared using either the spin casting or LB technique not only have important technological applications, but are also interesting from a scientific point of view in that the resulting polymer chain configurations are expected to be different in films prepared by these two methods. In spin-cast films, due to the force exerted along the radial direction during spinning, the polymer chains may under certain circumstances be frozen in a nonequilibrium state along that direction as the solvent evaporates (15). In LB films, due to the interaction between the subphase (water) and the hydrophilic groups of the polymer, the polymer chains are expected to exist in a partially oriented geometry. For single component ultrathin polymer systems, both spin-cast and LB films can be used to study the polymer chain configurations in constrained geometries. In addition, interchain diffusion, chain relaxation and chain-substrate interaction upon annealing are areas for potential investigation.

Most commonly used positive photoresists are composed of several components, including a polymer resin and small molecule photo-active compound (PAC) as well as the casting solvent. The chemical compatibility of the resin and the PAC is often rather poor, and aggregation of the two materials during casting is of potential concern. Aggregation of the resin or PAC could cause variations in local development rates, which would be most obvious at line edges. We have previously (15) investigated the effects of the casting solvent on the homogeneity of the spin-cast film. LB film formation allows us to investigate the interactions of these materials in a slightly different manner. The molecules are inherently more ordered due to the hydrophilic and hydrophobic interactions at the air/water interface. This ordering may affect the homogeneity of mixed films of novolac and PAC. The fact that we can control the novolac and PAC concentration in each monolayer will also allow us to investigate other film parameters such as the interdiffusion of the PAC and the polymer upon prebake and the "sphere of influence" of the PAC molecules in inhibiting dissolution.

One of the major obstacles to investigating ultrathin polymer films is the small amount of detectable sample material and, as a result, high instrument sensitivity is crucial. Although

polarized Fourier Transform Infrared Spectroscopy (13,14) has been used to study LB poly(octadecyl methacrylate) and poly(octadecyl acrylate) films, it was found that the signal-to-noise ratio decreases dramatically as the film thickness decreases from ~ 12 nm (6 layers) to less than 2 nm (one monolayer). Fluorescence spectroscopy has been used in the present study to investigate the microstructure of monolayer polymer films. With this technique, we are able to obtain the necessary signal-to-noise ratio to perform accurate measurements. Extrinsic fluorescence is capable of acting as a very sensitive probe of the polymer structure. A particular example is the use of pyrene excimer fluorescence, which has been employed in this study. The requirement for pyrene excimer formation is that two pyrene groups face each other in a sandwich arrangement at a separation distance of between 0.3 to 0.4 nm. Any structure changes on this scale will perturb the excimer forming sites and thus be detected.

### Experimental

Materials. The monodisperse atactic PMMA, which was used for the electron beam lithography and fluorescence spectroscopy studies, was obtained from Pressure Chemical. It has a weight average molecular weight ( $M_w$ ) of 188,100 and  $M_w/M_n < 1.08$ . Pyrenedodecanoic acid (PDA) for the fluorescence studies was obtained from Molecular Probes and used as supplied. Spectroscopic grade benzene purchased from J.T. Baker was used to prepare the PMMA and PMMA/PDA solutions as a spreading solvent.

The novolac sample, which was provided by Kodak, was synthesized from pure meta-cresol and formaldehyde. It has a weight average molecular weight of 13,000 and a very broad polydispersity of 8.5. The polymer was purified by two precipitations from tetrahydrofuran into hexane. The PAC was a naphthoquinone-1,2-(diazide-2-)-5-sulfonyl ester provided by Fairmount Chemical (Positive Sensitizer 1010). A hydroxyl substituted benzophenone is attached to the sulfonyl ester. The spreading solvent was isopropyl acetate, which was obtained from Aldrich Chemicals and used as received.

Substrates and LB film Preparation. The substrates used in the electron beam lithography studies consisted of 50-nm chromium (Cr) films evaporated over 100-nm thermally grown silicon oxide on 4-inch silicon wafers. The Cr and oxide layers provide an excellent contrast for evaluating etched Cr patterns with both optical and scanning electron microscopes (SEM). The substrates for the optical exposures were 3-inch silicon wafers upon which 50-nm chromium films had been evaporated. Three-inch quartz wafers obtained from Shin-Etsu Chem. Co. were used as substrates for the fluorescence measurements. The substrates were cleaned by immersion in a 9/1- $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$  solution at 120 °C for 20 min, followed by six cycles of deionized water rinsing and a final spin drying under a nitrogen ambient.

The LB film depositions were performed using a Joyce-Loebl Langmuir Trough IV equipped with a microbalance for measurement of the surface pressure by the Wilhelmy plate method. Filtered deionized water with a pH of 7 was used for the subphase. For the electron beam lithography study, PMMA was spread on the water surface from a dilute benzene solution (~ 10 mg PMMA in 20 ml benzene). The novolac/PAC mixtures were spread from solutions (~ 20 mg solids in 10 ml solvent) of isopropyl acetate. For the fluorescence studies, the PMMA/PDA mixture was spread on the water surface from a dilute benzene solution (1.75 mg PDA and 8.33 mg PMMA in 20 ml benzene). Prior to compression, a 20 min interval was allowed for solvent evaporation. The Langmuir film was compressed to the desired transfer pressure at a rate of 50  $\text{cm}^2/\text{min}$ , followed by a 20 minute equilibration period. The Cr-coated silicon wafers and quartz wafers were immersed into the subphase before the PMMA was spread on the water surface. The first monolayer of PMMA was transferred during the first upstroke of the substrate, at the speed of 2 mm/min.

Electron Beam Exposure. Single component LB PMMA films transferred at 5, 11, 15, and 17 dyn/cm, with thicknesses 0.9 nm (1 layer) to 15.3-nm (17 layers), have been prepared and investigated as high resolution electron beam resists by exposure with a modified Perkin Elmer

MEBES I pattern generation system. The MEBES exposures were performed at a 20 MHz address rate, 10 kV accelerating voltage,  $1/8\text{ }\mu\text{m}$  beam diameter and address size, and a 6 nA beam current resulting in a dose of  $2\text{ }\mu\text{C}/\text{cm}^2$  per scan. Equal line-space patterns with nominal feature sizes from  $1.25\text{ }\mu\text{m}$  down to  $0.125\text{ }\mu\text{m}$  were written. The dose ranges for this study were 1 - 200  $\mu\text{C}/\text{cm}^2$ . After exposure PMMA was developed in a 3:7 2-ethoxyethanol:methanol solution for 13 s. Prebaking and postbaking conditions were  $100^\circ\text{C}$  for 2 hours and  $90^\circ\text{C}$  for 30 min, respectively. Following the postbaking process the samples were put in a Cr etching solution (Cyantek CR-14) for 30 s to transfer the resist pattern to Cr. The samples were then examined with a scanning electron microscope (SEM).

Optical Exposure. Multicomponent LB films were prepared from solutions of novolac/PAC varying in concentration from 5 - 50 wt% PAC, and transferred at 2.5 - 10 dyn/cm. The films were composed of 15 - 20 monolayers, with an average film thickness of 30 nm, as measured by ellipsometry. Exposures were performed with a Canon FP-141 4:1 stepper (primarily g-line exposure) at an exposure setting of 5.2 and with a fine line test reticle that contains line/space patterns from 20 to  $1\text{ }\mu\text{m}$  (40 to  $2\text{ }\mu\text{m}$  pitch). They then were then developed in 0.1 - 0.2 M KOH, depending on the PAC content. The wafers received a 20 min  $120^\circ\text{C}$  post development bake to improve adhesion to the Cr. Finally, the Cr was etched in Cyantek CR-14 chromium etchant, and the resist and Cr images were examined by SEM.

Fluorescence Measurement. Fluorescence spectra were measured on a Spex Fluorolog 212 spectrofluorometer equipped with a 450 W xenon arc lamp and a Spex DM1B data acquisition station. Spectra were recorded in the front-face illumination mode using 343 nm as the excitation wavelength. Single scans were performed using a slit width of 1.0 mm. PDA fluorescence emission spectra were recorded from 360 to 600 nm, with the monomer and excimer fluorescence measured at 376.5 and 485 nm, respectively. Monomer and excimer peak heights were used in the calculation of the ratio of excimer to monomer emission intensities ( $I_e/I_m$ ). Excitation spectra were



recorded from 300 nm to 360 nm and monitored at 376.5 and 500 nm for the monomer and excimer excitation, respectively.

## Results

Electron Beam Lithography. LB PMMA films with thicknesses greater than 6.3 nm withstood the 50-nm Cr etching and allowed the patterns to be transferred from the resists into Cr films. Fig. 1 is an example of the patterns in Cr employing a 8.1 nm (9 layer) LB PMMA film, transferred at 15 dyn/cm, as a positive electron beam resist. Resist films prepared at different transfer pressures did not appear to differ substantially in their lithographic performance. Those films thinner than 4.5 nm (5 layers) proved unsuitable for withstanding the chromium etch once they had been cycled through MEBES (even though nominally unexposed).

Optical Lithography. For the novolac/PAC films, the PAC concentration was varied rather than the film thickness. Films with 5 % PAC could not withstand the Cr etchant. Films with 10 and 20 % PAC withstood the etchant and produced resolvable 1x1  $\mu$ m arrays (Fig. 2). The dose and development conditions would have to be optimized to achieve lines of the proper dimensions. Development of the films with 40 - 50 % PAC yielded observable resist images, but these images could not be replicated by Cr etching. An organic layer apparently remained in the bottom of the images and inhibited dissolution. There are also small defects in the films with high PAC concentrations (40 - 50 %), which do not appear in the films with lower PAC concentrations (Fig. 3). Films prepared at various transfer pressures did not exhibit significant lithographic differences.

Fluorescence Measurements. LB monolayer PMMA films doped with 5 mol% PDA have been prepared at surface transfer pressures ranging from 1 to 17 dyn/cm. Examples of PDA emission and excitation spectra are given in Figs. 4 and 5 respectively. The fluorescence measurements on these films have been plotted in Fig. 6 as  $I_e/I_m$  vs. surface pressure.  $I_e/I_m$  increases as the surface

pressure increases, and decreases as the pressure passes some critical value ( $\sim 10$  dyn/cm). A summary of the results of the fluorescence excitation spectra is presented in Table I. The excitation spectrum, which is analogous to the absorption spectrum, is generated by monitoring the emission intensity at a specific wavelength as a function of excitation wavelength. From the excitation spectrum we can analyze the configurations of different absorbed species. All the excimer excitation spectra were red shifted ( $\sim 4$  nm) and broadened relative to that of the monomer.

## Discussion

Electron Beam Lithography. LB PMMA films with thicknesses of 6.3 nm (7 layers) are sufficient for patterning a Cr film suitable for photomask fabrication. For ultrathin PMMA films the resolution (see Fig. 1) is limited by the smallest spot diameter available on MEBES I ( $1/8$   $\mu$ m). However, it is not possible to obtain this resolution if a thicker resist ( $> 100$  nm) is used under the same exposure and development conditions, which demonstrates that ultrathin resists are able to minimize the proximity effect. Also, since the radius of gyration of 188,100 Mw PMMA is about 10 nm in the bulk, and the thickness of the 7 layer film (6.3 nm) is less than 10 nm, it is reasonable to assume there must be an alteration of chain configuration in the ultrathin films. This will be particularly true when the post-deposition baking temperature of the multilayer films is less than the glass transition temperature ( $115^\circ\text{C}$ ), as is the case for the present experiments. In such a case, interdiffusion of PMMA chains between the deposited layers may not result in chain configurations characteristic of the bulk.

Optical Lithography. Resist films can be prepared from LB films of polymer/small molecule mixtures. Fig. 7 gives a schematic representation of a Langmuir film of novolac and diazoquinone mixture. Single layers of novolac are substantially thicker ( $\sim 2$  nm) than PMMA monolayers ( $\sim 1$  nm) suggesting that it is not possible for the novolac to have all of the phenolic groups in contact with the water surface due to the polymer's branched structure. Images in the

novolac/diazoquinone films could be resolved images down to about the resolution limits of the optical exposure tool used ( $\sim 1 \mu\text{m}$ ). Future electron-beam and deep UV exposures will allow us to evaluate the resolution of submicron images.

The homogeneity of the components in the LB films may affect the uniformity of dissolution in the exposed regions; however, aggregation of the PAC or novolac would cause regions with slower or faster dissolution, respectively. If the aggregated regions reached  $\sim 0.2 \mu\text{m}$  or larger, they could create observable roughness on the edges of the developed and etched images. In general, the edges of the images appear to be quite smooth for PAC concentrations at or below 20 wt%, although at high concentrations (40 - 50 wt%) small ( $0.1 - 1 \mu\text{m}$ ) variations are observable in the films. These may be related to the aggregation of the film components. Larger defects up to several hundred microns and thickness variations also occur in all of the films. It is not clear if these are directly related to aggregation, as thickness variations occur in films of pure novolac also.

Fluorescence Measurements. When the PMMA/PDA mixture forms a Langmuir film, the hydrophilic C=O groups of PMMA are expected to be directed toward the water phase with the chain backbone lying generally parallel to the water surface. The COOH groups of PDA are also expected to be directed toward the water with the long aliphatic chain and pyrene groups directed upward. Upon compression of the Langmuir film, the PMMA chains presumably become more compact and finally collapse. The collapse pressure of PMMA has always been a controversial issue in the literature. This has arisen because of different definitions and methods of determining collapse pressure, and different stereoregularity of the PMMA. Stroeve et al. (16) provides a detailed discussion of these points. They suggest that for Langmuir layers of syndiotactic PMMA ( $M_w \sim 100,000$ ) there are two important regimes: a regime where reversible loss becomes important, at about 15 dyn/cm, and a regime where there is an irreversible collapse of the Langmuir layer, at surface pressures greater than or equal 34 dyn/cm. While the reversible loss mechanism must be associated with some of the polymer being forced out of the monolayer, this layer must be

available to be drawn back into the interface upon expansion of the Langmuir layer. For the atactic-PMMA ( $M_w \sim 188,100$ ) used in this study, these two regimes were observed from the pressure-area measurements.

5 mol% PDA was used as a probe to detect structural changes in the PMMA matrix. As the pressure increases, the two dimensional surface concentration of PDA increases and thus the probability of intermolecular excimer formation will be enhanced, causing  $I_e/I_m$  to rise. However, once the pressure exceeds 10 dyn/cm,  $I_e/I_m$  starts to decrease indicating that the structure of the excimer has been influenced by microstructural changes in the polymer matrix. The excitation spectra of PDA at different surface pressures indicate that the extent of the red shift (excimer vs. monomer), which is due to the ground state interaction of the dyes, is not influenced by the surface pressure in the range 0 - 17 dyn/cm. This suggests that the probe molecules are not unduly constricted as the inter/intra chain voids shrink in size during compression. In other words, as the pressure increases, the voids become smaller and consequently  $I_e/I_m$  increases. However, despite the fact that the probes are forced to occupy a smaller area, they are not being constrained to the extent that they experience a change in ground state interaction. As the pressure surpasses  $\sim 10$  dyn/cm, the polymer chain may start to buckle and form loops that extend above the monolayer, thereby being disruptive to excimer formation in this region. No clear picture on the molecular level is presently available. However, the spirit of our concept is contained in the highly schematic representation of Fig. 8.

### Summary

Ultrathin LB PMMA and novolac/diazoquinone films have been demonstrated to act as high resolution electron beam and optical resists, respectively. Structural rearrangements in the LB PMMA films have been observed by using fluorescence spectroscopy. However, this rearrangement did not appear to influence the lithographic performance when seven or more layers of LB PMMA films were used as the resist. A more comprehensive study of the relationship

between lithographic performance and LB film structure is currently underway.

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Table I. Summary of the Results of PDA Fluorescence Excitation Spectra (188K Mw PMMA)

Surface Pressure (dyn/cm)	<sup>a</sup> $\lambda_{\text{Max}}$ (nm)		Peak Broadening <sup>b</sup>	
	Excimer Exc.	Monomer Exc.	Excimer Exc.	Monomer Exc.
2	348	344	1.18	1.69
4	348	344	1.26	1.73
6	347.5	344	1.45	2.06
8	347.5	344	1.42	1.95
10	348	344	1.49	2.14
12	347.5	344	1.38	1.95
14	347.5	344.5	1.50	2.17
16	347.5	344.5	1.51	2.26

a.  $\lambda_{\text{Max}}$  is the wavelength at which the global maximum peak intensity of the PDA excitation spectrum occurs.

b. Peak Broadening is defined as the ratio of the intensity of the maximum peak of the PDA excitation spectrum to the intensity of its adjacent local minimum.

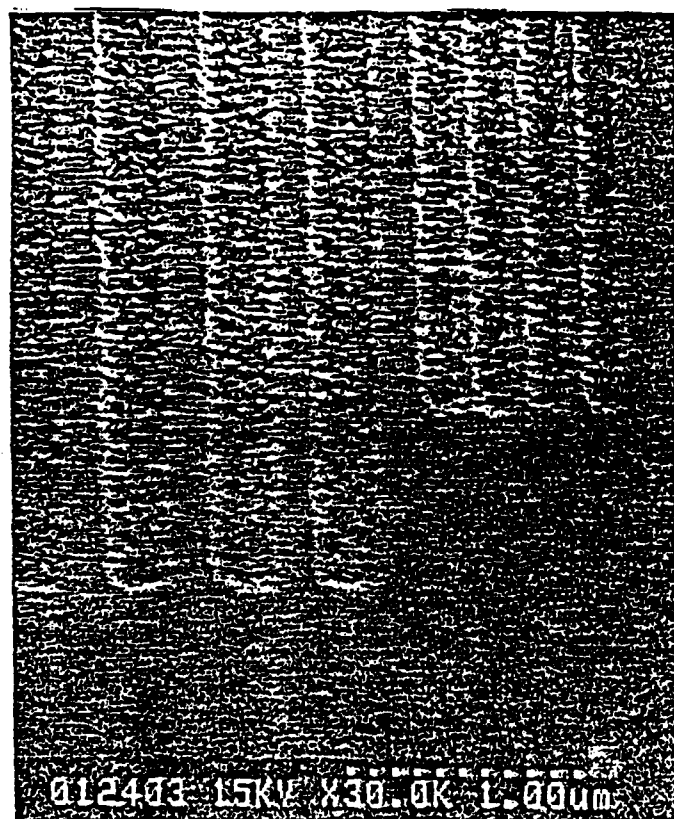


Fig. 1 Patterns in 50 nm Cr film employing a 8.1 nm (9 layers) LB PMMA film as resist, exposed with a MEBES I system at 10 kV accelerating voltage,  $1/8 \mu\text{m}$  beam diameter and address size, 6 nA beam current, and with a dose of  $80 \mu\text{C}/\text{cm}^2$ .



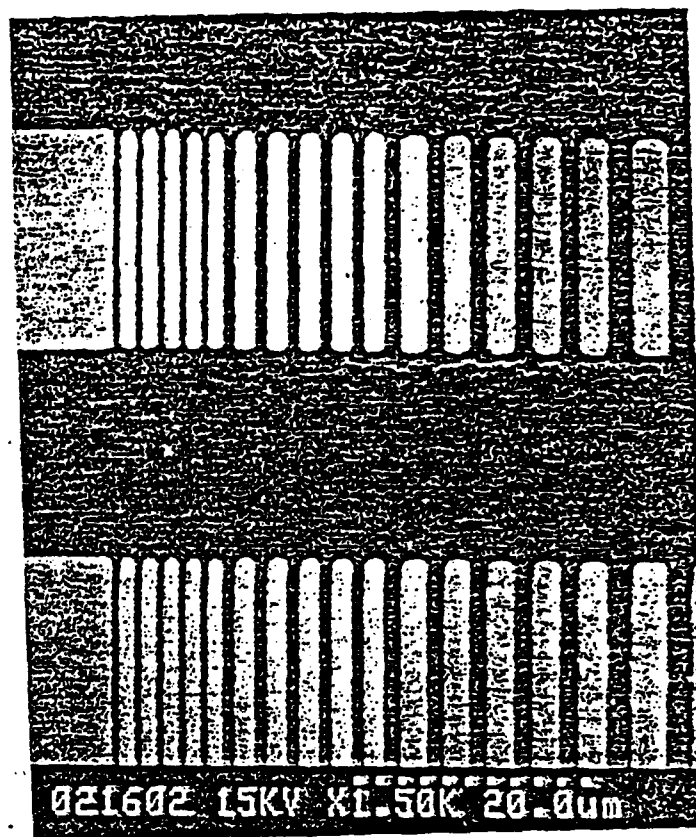
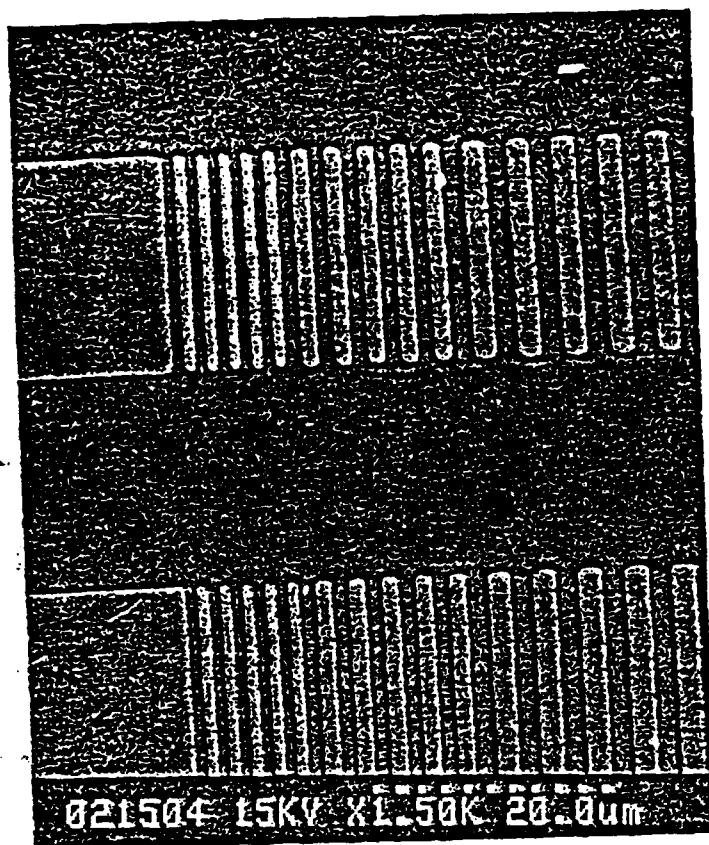


Fig. 2 Patterns in 50 nm Cr films employing 15 layers ( $\sim 30$  nm) of LB novolac/diazoquinone resist, with (a) 10 wt% and (b) 20 wt% diazoquinone. The smallest arrays are nominally  $1\text{ }\mu\text{m}$  lines-and-spaces.

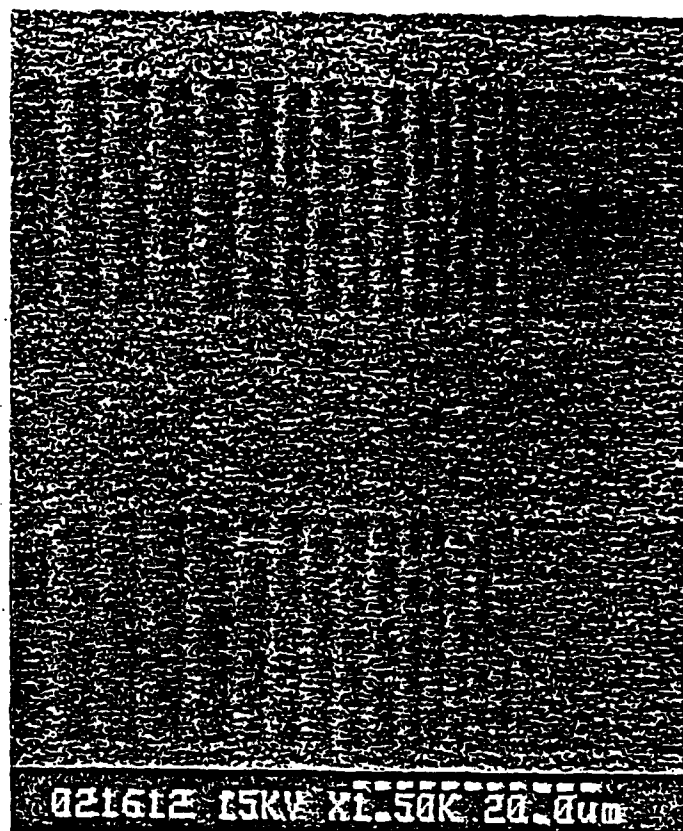
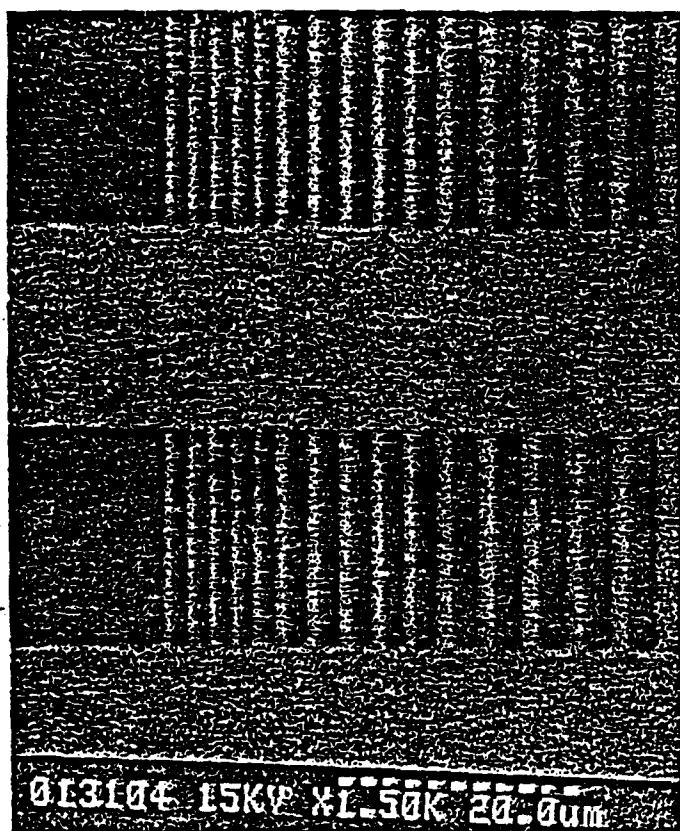


Fig. 3 Developed patterns in 15 layers of LB novolac/diazoquinone resist with (a) 20 wt% and (b) 50 wt% diazoquinone.

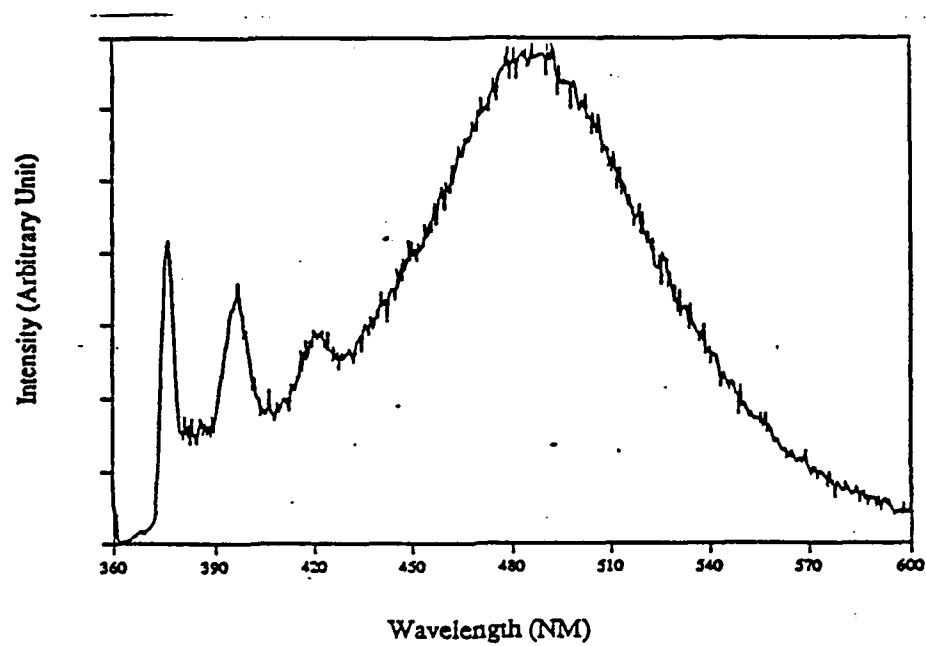


Fig. 4 Fluorescence emission spectrum of 5 mol% PDA in monolayer LB PMMA film transferred at 7 dyn/cm. The excitation wavelength is 343 nm.

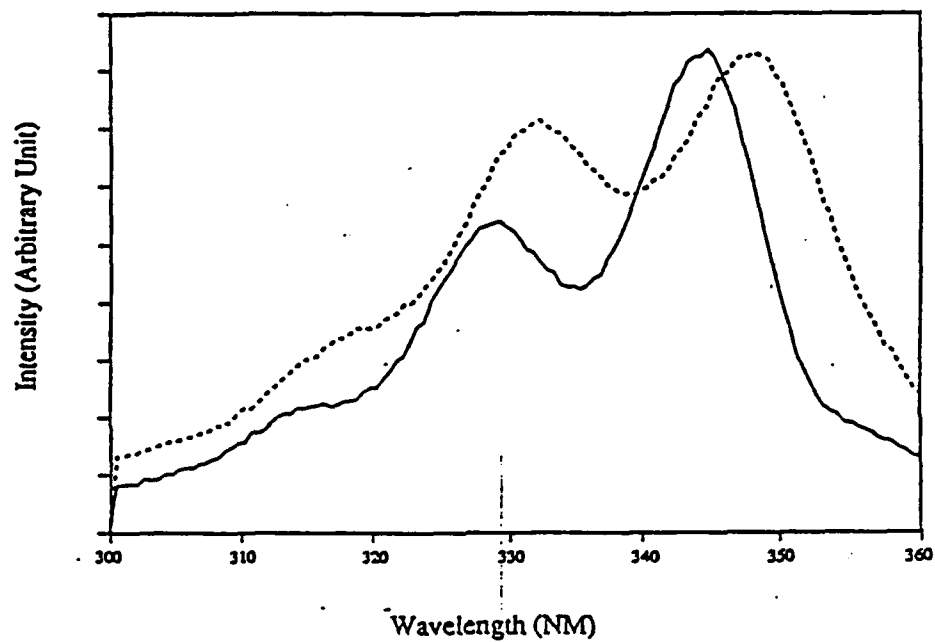


Fig. 5 Fluorescence excitation spectra of 5 mol% PDA in monolayer LB PMMA film transferred at 7 dyn/cm. The excimer excitation (dashed curve) was monitored at 500 nm and monomer excitation (solid curve) was monitored at 376.5 nm.

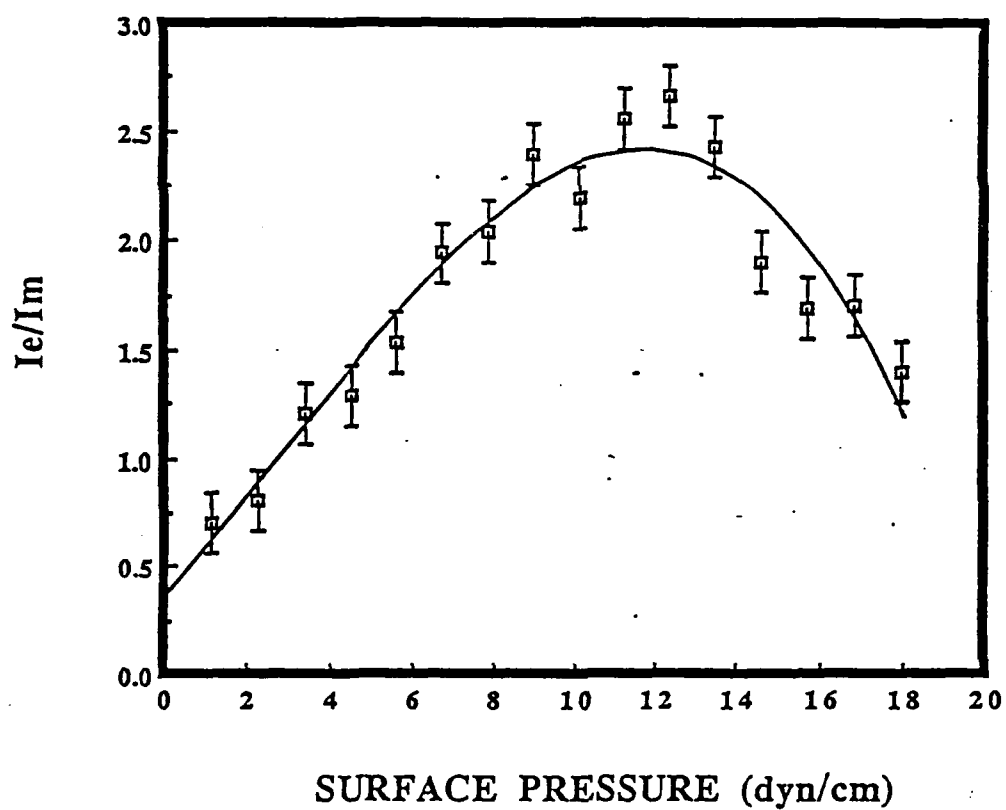


Fig. 6 Ratio of excimer ( $I_e$ ) to monomer ( $I_m$ ) fluorescence intensities of 5 mol% PDA in monolayer LB PMMA film as a function of transfer pressure.

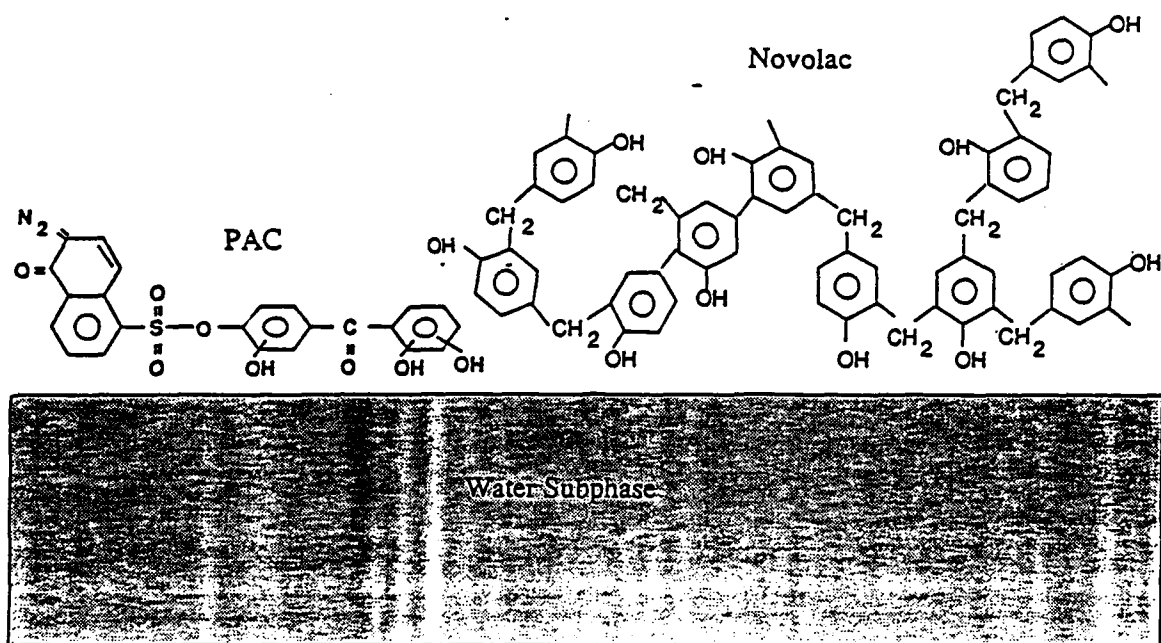


Fig. 7 Schematic of Langmuir film of mixtures of novolac and diazoquinone (PAC).

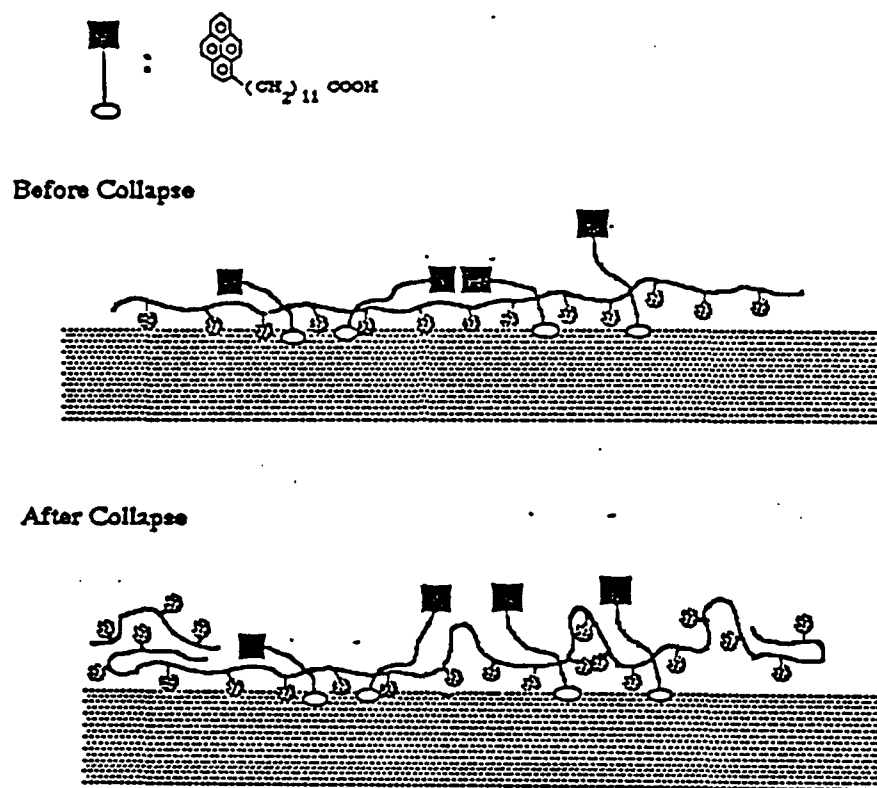


Fig. 8 Schematic of PDA dyes in monolayer Langmuir PMMA film on the water surface before and after the film collapse.